

Electronic Energy Levels of Weakly Coupled Nanostructures: C₆₀-Metal Interfaces

Jay D. Sau,^{1,2,*} J. B. Neaton,³ Hyoungh Joon Choi,⁴ Steven G. Louie,^{1,2} and Marvin L. Cohen^{1,2}

¹Department of Physics, University of California, Berkeley, California 94720, USA

²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

³Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

⁴Department of Physics and IPAP, Yonsei University, Seoul, 120-749, Korea

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A new approach based on density functional theory and the Anderson impurity model is developed to calculate charging energies and quasiparticle energy gaps of molecular systems weakly coupled to an environment. The approach is applied to C₆₀ adsorbed on Au(111) and Ag(100) surfaces, resulting in electronic structures that are in excellent agreement with recent experiments. Image-charge screening effects on molecular orbital energies are found to be of similar magnitude for the two surfaces, but charge-transfer screening and spin fluctuations also affect the Ag case due to a partially occupied C₆₀ orbital.

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Understanding and control of metal-organic contacts at the single-molecule level is a fundamental challenge in nanoscience, with important applications to future organic optoelectronic devices [1–3]. Recently, several experiments [4–12] have probed molecular systems adsorbed on metallic surfaces with the goal of improving the understanding of transport and optical properties. Scanning tunneling spectroscopy (STS), photoemission, and optical absorption spectroscopy measurements have reported significant changes in the electronic structure of individual molecules and molecular layers on metal surfaces as a function of coverage [9], substrate [7,10], molecule-substrate separation [8], and conformation [11]. Although these studies have resulted in remarkable progress, there remains a critical need for quantitative description of this key interface.

Fundamentally, the energetic positions of frontier molecular orbitals of a molecular adsorbate, relative to the Fermi level of a metal substrate, dictate interfacial electronic, optical, and transport properties [1]. Physical factors important to the molecular electronic level alignment include the size of the interface dipole (degree of charge transfer), level broadening and hybridization, and substrate polarization. Recently, the *quasiparticle gap* of a molecule weakly coupled to a metal surface, defined here as the difference between its affinity level [lowest unoccupied molecular orbital (LUMO)] and ionization level [highest occupied molecular orbital (HOMO)], was shown to be strongly renormalized by the polarization response of the metal surface to the added electron or hole, and strongly reduced from its corresponding value in the gas phase [13]. This is a nonlocal correlation effect which is not captured by electronic structure calculations based on density functional theory (DFT) with standard exchange-correlation functionals, such as those that use the local density approximation (LDA), and is thus entirely absent from mean-field Kohn-Sham eigenvalues. Many-body corrections to the Kohn-Sham eigenvalues within the *GW* approximation

[14–16] are well known to include such correlation effects [17], but these calculations become prohibitively expensive for complex systems with large numbers of atoms.

In this Letter, we develop a new approach that enables an efficient calculation of the quasiparticle gap of large molecules weakly coupled to a polarizable environment. Our approach consists of two steps. The first step is a new constrained DFT method to compute the charging energy, or screened Hubbard *U*, associated with the frontier orbitals and obtain quasiparticle energies including image-charge screening effects. In cases with a partially occupied molecular level, an Anderson impurity model (AIM) is constructed from the constrained DFT results as a second step to obtain a quasiparticle spectral function of the molecule that also includes screening due to transferred charge. We apply this two-step approach to find the positions of molecular energy levels and the quasiparticle (or HOMO-LUMO) gap of C₆₀ on Ag(100) and Au(111) surfaces, which were unavailable in previous DFT calculations [5]. Calculated results agree well with experiments for both C₆₀ on Au(111) and Ag(100), even though the quasiparticle spectra are quite different in the two systems. In particular, the charge-transfer screening has significant effect in only the Ag case, where the LUMO significantly overlaps the substrate Fermi energy.

In molecular systems, the quasiparticle energy gap can be defined as the difference between the ionization potential ($E[N-1] - E[N]$) and the electron affinity ($E[N] - E[N+1]$). Expressing both quantities as energy differences between neutral (*N* electron) and charged (*N* + 1 and *N* - 1 electron) systems, the gap E_g can be written as

$$E_g = E[N-1] + E[N+1] - 2E[N], \quad (1)$$

where $E[N]$ denotes the exact DFT total energy of a neutral system of *N* electrons. For molecules in a gas phase, total-energy approaches like the so-called Δ SCF method [18,19] are commonly used to determine the ionization potential

(IP) and electron affinity (EA), since the approximation $E[N] \approx E_{\text{LDA}}[N]$ and $E[N \pm 1] \approx E_{\text{LDA}}[N \pm 1]$ can result in good agreement with experiments [18,20]. However, if the molecule is coupled to an environment, such as a metal surface, this procedure is not well defined, since a clear separation between molecular and metallic states is not always possible.

To compute the IP and EA of a molecule weakly coupled to an environment, we develop an approach similar in spirit to the local spin density approximation plus Hubbard U (LSDA + U) method [21,22], an approach originally proposed for treating d orbitals weakly hybridized to itinerant electronic states. In LSDA + U [22], the screened charging energy, or the Hubbard U , of the weakly hybridized orbitals is defined by the difference between the LDA total energy and the exact DFT energy through the ansatz,

$$E[N + \delta n] \approx E_{\text{LDA}}[N + \delta n] + \frac{U^\pm}{2} |\delta n| (1 - |\delta n|), \quad (2)$$

where $N + \delta n$ is the occupancy of the isolated site, deviating by δn from an integer value N , and U^\pm is U^+ for $\delta n > 0$ and U^- otherwise.

From ensemble DFT arguments [23–25], the exact total energy is expected to be a piecewise linear function of occupancy, and the quadratic term in Eq. (2) corrects the pathological behavior of standard local exchange-correlation functionals with level occupancy. Equation (2) also guarantees $E[N + \delta n] \approx E_{\text{LDA}}[N + \delta n]$ for $|\delta n| = 0, 1$. Using Janak's theorem [26] and Eq. (2), we can derive expressions for the HOMO and LUMO eigenvalues as

$$\epsilon_{\text{LUMO}} = \left. \frac{\partial E[N + \delta n]}{\partial \delta n} \right|_{\delta n \rightarrow 0_+} \approx \epsilon_{\text{LUMO}}^{\text{LDA}} + \frac{U_{\text{LUMO}}}{2}, \quad (3)$$

$$\epsilon_{\text{HOMO}} = \left. \frac{\partial E[N + \delta n]}{\partial \delta n} \right|_{\delta n \rightarrow 0_-} \approx \epsilon_{\text{HOMO}}^{\text{LDA}} - \frac{U_{\text{HOMO}}}{2}, \quad (4)$$

where $\epsilon_{\text{LUMO}}^{\text{LDA}}$ and $\epsilon_{\text{HOMO}}^{\text{LDA}}$ are the LDA Kohn-Sham eigenvalues, and we have defined $U_{\text{LUMO}} = U^+$ and $U_{\text{HOMO}} = U^-$, respectively. From the linear dependence of the exact total energy on the occupancy, one can derive the relations $\text{IP} = -\epsilon_{\text{HOMO}}^{\text{LDA}} + U_{\text{HOMO}}/2$ and $\text{EA} = -\epsilon_{\text{LUMO}}^{\text{LDA}} - U_{\text{LUMO}}/2$. A definition of U adopted in other works [5] is related to the U_{HOMO} and U_{LUMO} defined above through $U = \text{IP} - \text{EA} - E_{g,\text{LDA}} = (U_{\text{HOMO}} + U_{\text{LUMO}})/2$. For noninteger occupations, we may set the second derivative of the exact DFT total energy to zero, using the piecewise linearity of the exact DFT total energy.

This results in expressions

$$U_{\text{HOMO}} = \frac{\partial \epsilon_{\text{HOMO}}^{\text{LDA}}}{\partial \delta n} \quad \text{for } \delta n < 0, \quad (5)$$

$$U_{\text{LUMO}} = \frac{\partial \epsilon_{\text{LUMO}}^{\text{LDA}}}{\partial \delta n} \quad \text{for } \delta n > 0 \quad (6)$$

proposing a constrained DFT method for computing U_α : we vary the total charge on the molecule by adding a small fraction of the charge density associated with the orbital α to the system, and then self-consistently update the remaining charge density. The change in the orbital eigenvalue versus the orbital charge can be monitored through peaks in the projected density of states (PDOS) on the molecule, and it determines the value of U .

We examine the C_{60} molecule on metal substrates as an application of our approach. This system has been studied experimentally and theoretically in detail [5,27,28]. In our present work, the C_{60} molecule is positioned with a hexagonal ring either at a Au(111) fcc hollow site or at the center of a hollow site with square planar symmetry on Ag(100) [29] and the relative positions are structurally relaxed. The DFT-LDA calculations were done with SIESTA [30] using a localized basis [31]. Calculated work functions are 5.40 and 4.59 eV for Au(111) and Ag(100), respectively, in good agreement with experiments [33].

First, we test our constrained DFT method with C_{60} in the gas phase and find the IP and EA to be 7.5 and 2.7 eV, respectively, in agreement with the ΔSCF method. Relative to our calculated Kohn-Sham energy gap of 1.6 eV, we obtain a value $U_{\text{HOMO}} = U_{\text{LUMO}} = U = 3.2$ eV for gas phase C_{60} . These results also agree well with measurement (7.8 eV [34] for the IP and 2.7 eV [35] for the EA) except that U is underestimated by 0.3 eV. As will be seen later, the IP-EA gap is also underestimated for the C_{60} molecule on Au(111) by 0.3 eV. Since the latter differs from the gas-phase gap predominantly because of image-charge screening correlations, we expect the amount by which U is underestimated by ΔSCF to be environment independent. This observation can be used to improve calculations for molecules where gas-phase data are available.

To compute the charging energy U_α for a C_{60} frontier orbital α on a metal surface, we transfer a fraction of charge from the substrate to the molecular orbital α , keeping the whole system neutral to avoid a spurious charge layer on the back side of the slab. A Coulomb truncation at a cutoff radius of 18 Å avoids intersupercell interaction while including the image-charge response without affecting the substrate energetics. The method, when applied to a benzene molecule oriented flat on a graphite surface [13], yields a reduction in the HOMO-LUMO gap of 3.15 eV from the gas-phase value, in excellent agreement with a previous GW calculation [13].

The calculated charging energy U for C_{60} on Au(111) and Ag(100) as a function of the molecule-substrate distance (Fig. 1) increases steadily with the distance of the molecule from the substrate in a way consistent with previous work based on the image-charge screening [5,13,36]. The electrostatic interaction between the charge on the substrate and the charge on the C_{60} accounts for the reduction in U further supporting the image-charge picture. Unlike in the case of benzene on graphite, the large polar-

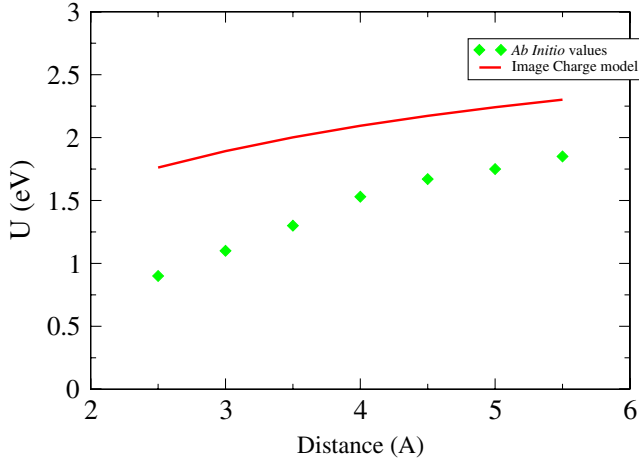


FIG. 1 (color online). Charging energy of the C_{60} molecule as a function of the molecule-substrate distance. Dots are results of our constrained DFT calculations for C_{60} on Au(111) [similar results are obtained for C_{60} on Ag(100)], and the solid line is a simple estimate with a point image charge, taking the image plane to be 1 Å [13,39] above the outermost atomic plane of the substrate.

izability of C_{60} causes a larger renormalization of U for C_{60} on metal substrates than expected from the simple image-charge model [13].

For both C_{60} on Ag(100) and Au(111), on including the aforementioned 0.3 eV correction, our constrained DFT method predicts a value $U = U_{\text{HOMO}} = U_{\text{LUMO}} = 0.9$ eV (Table I) in good agreement with STS data for the Au(111) case ($U = 1.0$ eV) [5]. However, the value observed in experiments is significantly smaller for the Ag case ($U = 0.4$ eV) [5], suggesting an additional screening mechanism due to charge transfer. To explore this, we represent the molecule-metal system by an AIM [37], with parameters obtained from the constrained DFT calculations described above and solve it within a GW approximation. Within this approach, the Green function for the molecule is given by

$$G_i(\omega + \mu) = [\omega - \epsilon_i - U_0 n - \delta \Sigma_i(\omega) + i\gamma_i \text{sgn}(\omega)]^{-1} \quad (7)$$

where i indicates a LUMO or HOMO level, μ is the Fermi energy of the substrate, and ϵ_i and γ_i are the HOMO or LUMO position relative to the Fermi level determined from the first step and the broadening of the i th level in the PDOS from LDA when the molecule is neutral. The level broadening $\gamma_i = 0.1$ eV is found to be energy independent in the relevant energy window consistent with the relatively flat substrate DOS. In the Au(111) case all three LUMO levels are calculated to be at $\epsilon_i = 1.0$ eV while in the Ag(100) case the levels are split into a single level $\epsilon_i = 0.05$ and a doublet at $\epsilon_i = 0.30$ eV. U_0 is the effective on-site Coulomb interaction seen by the molecular orbitals in the AIM which includes all of the screening effects apart from the charge transfer and was calculated to be 0.9 eV for both Ag and Au after including the 0.3 eV correction described. We note the dimensionless interaction strength $u = U_0/\pi\gamma_i = 2.8$ is in the range where the GW approximation [38] is valid quantitatively.

The total number n of electrons on the LUMO of the C_{60} molecule is given by $n = \sum_{\text{spin}} \int \frac{d\omega}{2\pi} A(\omega) - n_{\text{HOMO}}$ from the total spectral function, $A(\omega) = \sum_i (1/\pi) \text{Im}[G_i(\omega + \mu)]$, where n_{HOMO} is the number of electrons in the fully occupied HOMO. Within the GW approximation, the self-energy is given by $\delta \Sigma_i = iG_i(W - U_0)$ [14], using the screened interaction $W(\omega) = U_0/[1 - P(\omega)U_0]$ in the spin-independent case for completely filled orbitals and $W(\omega) = U_0 + U_0^2 P(\omega)/2[1 - U_0^2 P(\omega)^2/4]$ in the spin-dependent case for partially filled orbitals [38]. The additional polarizability $P(\omega)$ arising from charge transfer is the product of the molecular Green functions and originates almost entirely from the LUMO state. The matrix elements of the relatively long-ranged Coulomb interaction between the orthogonal LUMO states are small and therefore ignored, thus neglecting changes in intramolecular polarizability.

The quasiparticle levels are determined from the peak positions in the self-consistently calculated total molecular spectral function $A(\omega)$. From the above calculation we find the LUMO occupancy n to be $0.4e$ in the Ag(100) case, and a further screening of the charging energy from 0.9 to 0.5 eV and an increase in the LUMO splitting from the LDA value of 0.25 to 0.5 eV, as shown in Fig. 2, in good agreement with experiment (see Table I). The spin-independent GW approximation underestimates the LUMO splitting by 0.2 eV, indicating the significant role played by spin fluctuations in the Ag case.

To summarize, we develop here a new method to describe the image-charge and charge-transfer screening effects on the quasiparticle energy levels in a molecule weakly coupled to a metallic surface. Our method is based on a constrained DFT calculation and a GW approximation of an Anderson impurity model, and it is successfully applied to C_{60} molecules on Au(111) and Ag(100) sur-

TABLE I. Summary of results: Energies are in eV, $\Delta E_{\text{LUMO}}^{C_{60}}$ refers to the splitting of the LUMO of C_{60} when placed on Ag(100) and $\Delta E_g^{\text{benzene}}$ refers to the change in the HOMO-LUMO gap of benzene. In the middle column, 0.3 eV has been added to the U values for C_{60} as described in the text.

| | Present | Present (corrected) | Previous |
|---|---------|---------------------|-------------------|
| $U^{C_{60}}/\text{Au}$ | 0.6 | 0.9 | 1.0 ^a |
| $U^{C_{60}}/\text{Ag}$ | 0.3 | 0.5 | 0.4 ^a |
| $E_{\text{LUMO}}^{C_{60}}/\text{Au}$ | -4.25 | -4.4 | -4.3 ^a |
| $\Delta E_{\text{LUMO}}^{C_{60}}/\text{Ag}$ | 0.30 | 0.55 | 0.5 ^a |
| $\Delta E_g^{\text{benzene}}/\text{graphite}$ | 3.15 | - | 3.16 ^b |

^aSTS data [5]

^b GW calculations [13]

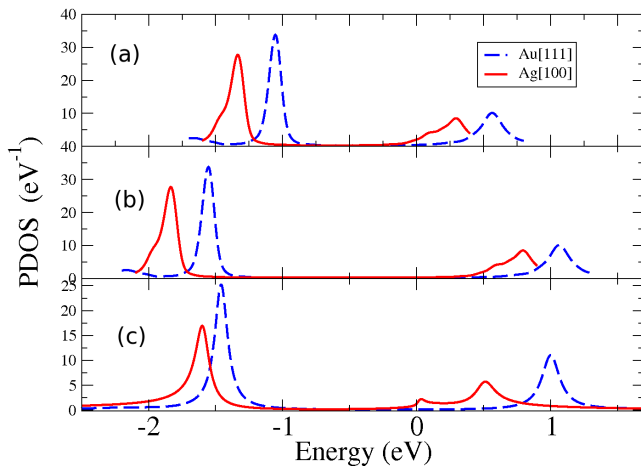


FIG. 2 (color online). PDOS of C_{60} on Ag(100) and Au(111): (a) standard LDA results (molecule placed at the relaxed distance), (b) LDA results (corrected by 0.3 eV) shifted by the DFT + screened U method described in the text, and (c) the total spectral function including DFT + U and our Anderson impurity model for charge-transfer screening.

faces, resolving the apparent difference of the electronic structures observed in experiments. We expect that our method can be applied, in general, to other molecular systems weakly coupled to metallic substrates and other environments, where the frontier orbitals can be described as a single-site multiorbital model whose Coulomb interaction kernel can be described adequately by the U parameters.

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*jay@civet.berkeley.edu

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